OXIDATION OF RESIDUAL METHANE FROM VNG VEHICLES OVER CO$_3$O$_4$-BASED CATALYSTS: COMPARISON AMONG BULK, AL$_2$O$_3$-SUPPORTED AND Ce-DOPED CATALYSTS

A. Choya, B. de Rivas, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, R. López-Fonseca

1   **OXIDATION OF RESIDUAL METHANE FROM VNG VEHICLES**

2   **OVER Co$_3$O$_4$-BASED CATALYSTS: COMPARISON AMONG**

3   **BULK, Al$_2$O$_3$-SUPPORTED AND Ce-DOPED CATALYSTS**

4

5   Andoni Choya, Beatriz de Rivas, Juan Ramón González-Velasco

6   Jose Ignacio Gutiérrez-Ortiz, Rubén López-Fonseca*

7

8   Chemical Technologies for Environmental Sustainability Group,

9   Department of Chemical Engineering, Faculty of Science and Technology,

10   University of the Basque Country UPV/EHU, PO Box 644, E-48080 Bilbao, Spain

11

12

13   *Corresponding author:

14   Phone: +34-94-6013485

15   Fax: +34-94-6015963

16   E-mail address: ruben.lopez@ehu.eus

17

ABSTRACT

Cobalt oxide based catalysts with three different active phase configurations, namely bulk, alumina supported and cerium-doped Co_3O_4 samples were examined for the complete oxidation of methane under conditions similar to those found in the exhaust of VNG engines. The structural and redox properties of the resulting catalysts were determined by N_2 adsorption-desorption, WDXRF, ICP-AES, X-Ray diffraction, temperature-programmed reactions, UV-vis-NIR DRS, XPS and Raman spectroscopy. Alumina-supported catalysts (10–40%wt. Co) were found to be less active, since the strong interactions between the alumina and the Co_3O_4 active phase were highly detrimental for the redox properties of these catalysts. On the other hand, doping with cerium (10%wt.) led to an increased inherent activity of the Co_3O_4 phase by distorting the spinel lattice, which resulted in improved structural and redox properties and enhanced mobility of the oxygen species within the spinel lattice. These catalysts were also stable over a prolonged period of time under both dry and humid conditions (150 hours).

Keywords: catalytic combustion, methane, cobalt oxide, cerium doping, oxygen mobility

1. Introduction

The use of natural gas as fuel for vehicles (also known as Vehicular Natural Gas or VNG) is considered a reliable alternative, with a well-established technology, that can serve as a transition technology in the way to cleaner H_2-based energy sources. VNG engines are between 10-20% more efficient than gasoline or diesel engines and have a lower environmental impact with limited NO_x and soot emissions [1-4]. Their main technical limitation lies in the release of residual methane, not burned in the engine, which is a powerful greenhouse effect gas.

Catalytic oxidation constitutes an attractive post-treatment strategy to convert methane into CO_2 and water. Unfortunately, it is a noticeably demanding process compared with the oxidation of other hydrocarbons such as propane or butane, due to its high chemical stability. This low reactivity determines the temperature of the process, which should not exceed a temperature threshold of 500 °C, since that is the thermal level of the exhaust gases from the engine. The mostly used catalysts on a commercial scale for VNG vehicles are based on supported noble metals, mainly palladium [5,6]. However, these catalysts, which can contain up to a 4% in weight of palladium, are expensive while their behaviour is negatively influenced by sintering and the presence of water in the reaction stream [7,8]. In this context, finding cheaper, alternative catalysts with an appropriate performance has become an interesting challenge that has the potential to reduce the cost of post-treatment systems for exhaust gases and contribute to increase the attractiveness of VNG engines as well.

Cobalt spinel oxides, like Co_3O_4, have been demonstrated to exhibit a high activity for methane catalytic combustion, and are therefore considered good alternative candidates to noble metal based catalysts, owing to their relatively low cost, high thermal and hydrothermal stability and selectivity to CO_2 [9,10]. However, the specific

61 physicochemical properties of these catalysts are highly dependent on the specific

62 configuration of the active phase, that is, whether the Co_3O_4 is a bulk phase, supported

63 on a porous media, or mixed with other elements. Pure bulk Co_3O_4 catalysts take

64 advantage of the excellent redox properties of this material, which allow for a good

65 mobility of the oxygen species and reducibility. However, their structural properties are

66 usually very poor when using conventional synthesis methodologies (precipitation or

67 direct calcination), with low specific surface areas and large crystallite sizes [11,12].

68 Better textural properties can be obtained with solvothermal or hard-template-based

69 routes [13-16]. In a simpler way, an increased available metallic surface area and

70 improved structural properties can be obtained by depositing the Co_3O_4 phase over the

71 surface of a porous media. This strategy has been reported to enhance the inherent

72 catalytic activity of Co_3O_4 in some cases [17,18], but, in other cases, the interactions

73 between cobalt oxide and the support can be detrimental owing to their negative impact

74 on the redox properties [19]. For example, when alumina is used as a support the

75 formation of $CoAl_2O_4$ often occurs. This undesired phase fix a certain amount of cobalt

76 species due to its high stability. Therefore, a fraction of deposited cobalt species is not

77 able to participate in the Co^{3+}/Co^{2+} redox cycle. On the other hand, doping the bulk Co_3O_4

78 with another metallic element can improve its textural and redox properties [20,21]. The

79 properties of the resultant catalysts strongly depend on various parameters such as the

80 composition or the presence of segregated or undesired phases [22].

81 Up to now, various cobalt-based catalysts with the described three configurations have

82 been profusely examined for the complete oxidation of methane [9,17,23-28]. However,

83 the different routes employed for catalysts synthesis and the wide range of operation

84 conditions chosen for catalytic evaluation make the comparison of their corresponding

85 performance and properties a particularly difficult task [29]. To the best of our

86   knowledge, no systematic analysis of the three type of catalysts under the same conditions

87   has ever been attempted. Thus, in the present work, these three configurations have been

88   implemented for the design of Co_3O_4 catalysts for methane catalytic oxidation. More

89   specifically, various bulk Co_3O_4 samples were prepared by simple calcination and

90   precipitation. Secondly, a series of Co_3O_4 catalysts supported on alumina with varying

91   cobalt content in the range 10–40%wt. were examined. Lastly, as for doped Co_3O_4

92   catalysts, several samples modified by cerium, with a content between 5 and 20%wt.,

93   were synthesised. Along with a detailed characterisation of the physicochemical

94   properties of these catalysts, by means of a wide number of analytical techniques

95   including BET measurements, XRD, WDXRF, ICP-AES, UV-vis-NIR DRS, Raman

96   spectroscopy, XPS, H_2-TPR and CH_4-TPRe, this work presents kinetic data that were

97   correlated with the key catalytic properties of each type of catalyst. Also, attention has

98   been paid to examining the catalytic stability during a prolonged time interval under both

99   dry and humid conditions.

100

101   **2. Experimental**

102   *2.1.   Catalysts preparation*

103   Bulk Co_3O_4 catalysts were prepared following two different routes, already described

104   elsewhere [30]. The first route was a simple calcination in static air of two different cobalt

105   precursors, namely cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) and

106   cobalt (II) hydroxycarbonate ($2CoCO_3 \cdot 3Co(OH)_2 \cdot xH_2O$, Panreac). The resulting samples

107   were denoted as DC and HC, respectively. The second route consisted of an aqueous basic

108   precipitation of a cobalt precursor, resulting in the formation of cobalt hydroxycarbonate.

109   A solution of Na_2CO_3 1.2M was added drop-by-drop to 100 mL of $Co(NO_3)_2 \cdot 6H_2O$ 0.5M,

110   while the temperature was kept constant at 80 °C, until pH 8.5 was attained. The obtained

111   precipitates were collected and washed thoroughly with at least 5 litres of water, to wash

112   off all the sodium ions which are known to be especially detrimental for the activity of

113   oxidation catalysts [31]. The sample was labelled as CC. Finally, a commercial bulk

114   Co_3O_4 sample (Alfa Aesar) was used as reference. This sample was denoted as COM.

115   Supported Co_3O_4/Al_2O_3 catalysts were prepared by a precipitation route following the

116   same methodology as the CC catalyst, but adding γ-Al_2O_3 (Saint Gobain Norpro SA

117   6173), previously stabilized at 850 °C for 4 h in static air. The selected metallic Co

118   loadings were 10, 20, 30, 35 and 40wt%. These samples were denoted as xCo/Al_2O_3

119   where x stands for the nominal cobalt loading. For comparative purposes, a bulk $CoAl_2O_4$

120   sample was also obtained by a precipitation route, where a cobalt salt ($Co(NO_3)_2 \cdot 6H_2O$)

121   and an aluminium salt ($Al(NO_3)_3 \cdot 9H_2O$) with stoichiometric proportions were

122   precipitated by the drop-by-drop addition of Na_2CO_3 1.2M, until pH 9 was achieved.

123   Cerium-doped bulk Co_3O_4 catalysts were prepared by a precipitation route, similar to the

124   route followed for the synthesis of the CC sample, but starting from adjusted mixtures of

125     $Ce(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ to obtain catalysts with nominal cerium loadings of

126   5, 10, 15 and 20wt%, which corresponded to Ce/Co molar ratios of 0.03, 0.06, 0.10 and

127   0.14, respectively. The samples were named as xCe/Co_3O_4 where x is the nominal cerium

128   content. In addition, a sample of pure CeO_2 was prepared using the same route. Again,

129   the obtained precipitates were collected and washed thoroughly with water. All catalyst

130   precursors were dried in static air at 110 °C for 16 hours and subjected to calcination in

131   static air to produce the final catalysts. The calcination protocol was defined on the basis

132   of the results obtained from a previous thermogravimetric analysis over the catalyst

133   precursors, and involved three heating steps, separated by 30-minute isotherms: an initial

134   step at 5 °C min^{-1} from room temperature to 125 ºC, an intermediate step at 1 °C min^{-1}

135   until 300 °C and a final step at 5 °C min^{-1} until 600 °C, which was then maintained for 4

136   hours. Exceptionally, the bulk $CoAl_2O_4$ sample was also calcined at 850 °C.

137   *2.2.   Characterisation techniques*

138   Textural properties of the catalysts were determined from the nitrogen-adsorption

139   isotherms at -196 °C obtained with a Micromeritics TriStar II apparatus. The specific

140   surface of the samples was obtained by the BET method, and the average pore size was

141   calculated using the BJH method. All samples were degassed prior to analysis on a

142   Micromeritics SmartPrep apparatus at 300 ºC for 10 hours with a N_2 flow.

143   The composition of the supported Co_3O_4/Al_2O_3 catalysts and the $CoAl_2O_4$ samples was

144   determined by Wavelength Dispersive X-Ray Fluorescence (WDXRF). From each

145   sample in powder form, a boron glass pearl was prepared by fusion in an induction micro-

146   furnace, by mixing the sample with the flux agent Spectromelt A12 (Merck) in an

147   approximate proportion of 20:1. Chemical analysis of each pearl was performed under

148   vacuum, using a PANalytical AXIOS sequential WDXRF spectrometer, equipped with a

149   Rh tube and three different detectors (gas flow, scintillation and Xe sealed). The

150   composition of Ce-doped catalysts was determined by ICP-AES in a Thermo Elemental

151   Iris Intrepid apparatus. The pretreatment involved the acid digestion of 5-10 mg of each

152   sample, followed by dissolution in 100 mL of Milli-Q water.

153   Structural properties of the catalysts were determined by X-Ray diffraction. XRD analysis

154   were performed on a X'PERT-PRO X-Ray diffractometer using Cu Kα radiation (λ =

155   1.5406 Å) and a Ni filter. The X-Ray tube was operated at 40 kV and 40 mA of current.

156   The samples were scanned from an initial value of 2θ = 5° to a final value of 2θ = 80°,

157   with a step size of 0.026° and a counting time of 2.0 seconds for each step. Phase

158   identification was performed by comparison of the obtained diffraction patterns with

159   JCPDS (Joint Committee on Powder Diffraction Standards) database cards. Occasionally,

160   a longer counting time (26.8 s) was applied to perform a detailed XRD analysis over the

161   supported Co_3O_4/Al_2O_3 and Ce-doped catalysts. The cell size of the Co_3O_4 phase was

162   obtained by profile matching of the detailed XRD patterns using FullProf.2k software.

163   Redox properties and Co species distribution was investigated by means of different

164   techniques. Temperature-programmed reduction with hydrogen (H_2-TPR) was performed

165   on a Micromeritics Autochem 2920 apparatus, using a $5\%H_2/Ar$ mixture as the reducing

166   gas. The analysis protocol involved an initial pre-treatment step with a $5\%O_2/He$ mixture

167   at 300 °C for 30 minutes. The aim of this step was to remove impurities and/or water that

168   could be retained on the surface of the samples while at the same time fully restoring the

169   oxygen vacancies of the spinel lattice before the analysis of the reducibility. After cooling

170   down to room temperature with flowing He, the TPR experiment was performed, up to

171   600 °C for the bulk Co_3O_4 catalysts, 950 °C for the supported Co_3O_4/Al_2O_3 catalysts and

172    $CoAl_2O_4$ samples and 900 °C for the Ce-doped Co_3O_4 catalysts. The corresponding final

173   temperature was then maintained for 30 minutes. The water produced throughout the

174   whole experiment was eliminated using a cold trap, to avoid interference with the TCD

175   detector. Additional information regarding the reducibility of the catalysts was obtained

176   by means of temperature programmed reaction with a $5\%CH_4/He$ mixture in the absence

177   of oxygen (CH_4-TPRe) coupled to mass spectrometry (MKS Cirrus Quadrupole Mass

178   Spectrometer).

179   X-Ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS system

180   equipped with a Phoibos 150 1D analyzer and a DLD-monochromatic radiation source.

181   UV-vis-NIR diffuse reflectance (DRS) spectra of the samples was obtained on a Jasco V-

182   570 apparatus in the 200-2300 nm wavelength range. The analysis by Raman

183   spectroscopy was carried out by using a Renishaw InVia Raman spectrometer, coupled

184   to a Leica DMLM microscope. The excitation wavelength was 514 nm (ion-argon laser,

185 Modu-Laser). The spatial resolution was 2 microns. For each spectrum 20 seconds were

186 employed and 5 scans were accumulated with the 10% of the maximum power of the 514

187 nm laser in a spectral window of 150-1200 cm^{-1}.

188

189 *2.3.   Catalytic activity determination*

190 Catalytic activity tests were performed in a bench-scale fixed bed reactor, Microactivity

191 modular laboratory system manufactured by PID Eng&Tech S.L., operated at

192 atmospheric pressure and monitored by computer. The reactor was a stainless steel

193 (Hasteloy X) tube, manufactured by Autoclave Engineers, with an internal diameter of

194 8.55 mm and a length of 305 mm. The temperature inside the reactor was measured by a

195 multipoint K type thermocouple placed in the catalyst bed. For each reaction experiment,

196 1 g of catalyst granulated to a particle size of 0.25–0.3 mm was loaded into the reactor,

197 diluted with 1 g of inert quartz granulated to a particle size of 0.5–0.8 mm to improve gas

198 flow and heat distribution along the bed and avoid diffusional effects affecting the

199 reaction rate. A reactor diameter/particle diameter ratio (31) higher than 10 and a catalytic

200 bed length/particle diameter ratio (79) higher than 50 ensured that both by-pass and axial

201 dispersion effects could be neglected (Table S1, Supplementary material) Thus, an ideal

202 plug-flow in the reactor could be supposed.

203 The feed consisted of a gaseous mixture of 1%CH_4, 10%O_2 and N_2 as the balance gas.

204 The selected composition of the gas feed was comparable to that found in the exhaust of

205 VNG engines, which typically contains 0.5-1%CH_4 and 5-10%O_2. A total gas flow of

206 500 cm^3 min^{-1} was used, which corresponded to a gas hourly space velocity of 60,000 h$^-$

207 ^{1} approximately (300 mL CH_4 g^{-1} h^{-1}). Catalytic activity was measured from 200 to

208 600 °C. Conversion measurements and product profiles were taken at steady state each

209 25 °C, typically after 15 minutes on stream. The furnace temperature was programmed in

210 a stepwise progression. Each temperature level was attained using a heating ramp of 1 °C

211 min^{-1}. Additionally, stability tests (1%CH_4, 10%O_2 and N_2 as the balance gas) in the

212 presence (10%H_2O) or absence of water vapour were carried out for a total time on stream

213 of 150 h at 450 ºC. Methane conversion was calculated by the difference between inlet

214 and outlet CH_4 concentrations. Inlet and outlet streams were analysed using an on-line

215 Agilent Technologies 7890N gas chromatograph equipped with a thermal conductivity

216 detector (TCD) and two columns: a PLOT 5A molecular sieve column for the analysis of

217 CH_4, O_2, N_2 and CO; and a PLOT U column for CO_2 analysis. Each chromatographic

218 analysis was performed in triplicate in order to check reproducibility, which was below

219 1%. To ensure that the obtained catalytic results were not affected by both mass and heat

220 transfer limitations, the criteria for intra-granular and extra-granular mass diffusion,

221 energy diffusion and temperature gradients were checked to be above the limit, according

222 to the Eurokin procedure [32,33]. It was therefore considered that catalytic activity results

223 were not significantly influenced by interphase transportation. The calculations are

224 summarised in Table S1 (Supplementary material).

225

226 **3. Results and Discussion**

227 *3.1.   Evaluation of bulk Co_3O_4 catalysts*

228 The textural properties of the bulk Co_3O_4 samples in terms of BET surface area, pore

229 mean diameter and pore volume are shown in Table 1. The surface area varied between

230 5 m^2 g^{-1} over the DC sample and 14 m^2 g^{-1} over the CC sample. This latter oxide also

231 exhibited the largest pore volume and smallest pore diameter, thus suggesting that the CC

232 route produces samples with better textural properties. The structural properties were

233 characterised by XRD, using the JCDPS files as a reference. For every sample, all

234 diffraction peaks, located at 19.0°, 31.3°, 36.8°, 44.8°, 59.4° and 65.2°, could be assigned

235   to a pure phase of mixed cobalt (II,III) oxide with spinel structure (JCPDS 42-1467). The

236   crystallite size, also included in Table 1, was estimated from the Full Width Half

237   Maximum (FWHM) of the characteristic peak located at 36.8°, which corresponded to

238   the (311) plane, by applying the Scherrer equation. It was found that the crystallite sizes,

239   in the 63−84 nm range, inversely correlated to their specific surface area. This relationship

240   was explained in terms of small Co_3O_4 crystallites exposing higher surfaces than larger

241   ones [34,35].

242   TABLE 1

243   The redox properties of Co_3O_4 were investigated by means of H_2-TPR. For all samples

244   the hydrogen consumption profiles (Figure 1) were relatively similar, showing a two-step

245   reduction process. The first hydrogen consumption peak, centred at 310 °C, was assigned

246   to the reduction of Co^{3+} to Co^{2+}; whilst the second reduction peak, located between 325

247   and 425 °C, was attributed to the reduction of Co^{2+} to metallic Co [36]. No other hydrogen

248   consumption was detected over 500 °C. It was therefore confirmed that the only reducible

249   phase present in all samples was Co_3O_4. After integration and quantitative evaluation of

250   the TPR profiles, the specific hydrogen uptake of each reduction step and the

251   corresponding ratio were computed, as shown in Table 1. The specific consumption of

252   the synthesised oxides was very similar to the theoretical value (16.6 mmol g^{-1}). As for

253   the ratio between the two uptakes, the CC sample gave the highest value (0.35). This was

254   slightly higher than the theoretical ratio (0.33)

255   FIGURE 1

256   On the other hand, XPS analysis could provide useful information about the distribution

257   of the reducible species on the surface of the spinel. For all bulk Co_3O_4 samples, Co 2p

258   spectra (Figure S1, Supplementary material) showed broad signals, thus suggesting the

259   presence of various cobalt species on the surface. In particular, the Co $2p_{3/2}$ signal could

260 be deconvoluted in at least five different contributions [37,38]. Hence, the two signals

261 located at lower binding energies, namely 779.5 and 780.7 eV, were attributed to Co^{3+}

262 and Co^{2+} cations associated with oxide O^{2-} anions, respectively, while the signal centred

263 at about 782.7 eV was attributed to the presence of CoO species on the surface. The

264 presence of this species was comparable on the four samples, around 5−10% of the total

265 amount of cobalt. Finally, the two signals located at higher binding energies (785.5 and

266 789.5 eV) were identified as the satellite signals from Co^{2+} and Co^{3+} ions, respectively

267 [39]. The O 1s spectra showed two different signals located at 529.8 and 530.8 eV,

268 respectively. The former was assigned to oxygen ions from the lattice (O_{latt}) while the

269 latter was attributed to adsorbed oxygen species on the surface (O_{ads}) [40]. From the

270 quantification of the signals, the Co^{3+}/Co^{2+} and O_{ads}/O_{latt} molar ratios (Table 1) could be

271 calculated. The relationship shown in Figure 2 evidenced that the higher the surface

272 Co^{3+}/Co^{2+} molar ratio, the higher the concentration of lattice oxygen species [37].

273   FIGURE 2

274 The catalytic activity of each bulk Co_3O_4 catalyst for the complete oxidation of methane

275 was assessed by defining their respective light-off curves. Since the calcination process

276 would stabilize the catalysts up to the calcination temperature, light-off curves were taken

277 between 200 and 600 °C. For each sample, three consecutive tests were performed. In all

278 cases, the second and third cycles were characterised by an identical light-off curve

279 (Figure 3). This revealed that the first cycle worked as a 'conditioning' cycle and, after

280 that, the catalysts became stable under the employed reaction conditions. On the basis of

281 the T_{50} (temperature required for 50% conversion) values the following trend was noticed:

282 CC>COM>HC>DC. This finding evidenced that precipitation was a more suitable

283 preparation methodology for bulk oxides. Note that in all cases the selectivity to CO_2 was

284 100%. The reaction rate of the catalysts was calculated at 375 °C under differential

285 conditions, this is to say, when the methane conversion was below 20%. The estimated

286 values were in the 1.07-1.85 mmol CH_4 g_{Co}^{-1} h^{-1} (Table 2). On the other hand, the integral

287 method was applied to estimate the apparent activation energy when considering a first

288 pseudo-order for methane and a zero pseudo-order for oxygen. The assumed reaction

289 orders were compatible with Mars–van Krevelen kinetics with an excess of oxygen,

290 which has already been proven to be the most plausible model for the catalytic oxidation

291 of methane and other hydrocarbons [18,41]. Conversions between 10 and 90% were fit

292 to the following linearized equation for the integral reactor (Equation 1)

293
$$\ln\left[-\ln\left(1-X\right)\right] = \ln\left[k_0 C_{CH_{4_0}}\left(\frac{W}{F_{CH_{4_0}}}\right)\right] - \frac{E_a}{RT} \tag{1}$$

294 where X is the fractional conversion of methane, k_0 is the pre-exponential factor of the

295 Arrhenius equation and W/F_{CH40} is the weight hourly space velocity. The goodness of the

296 numerical fit is shown in Figure S2 (Supplementary material) while the corresponding

297 values for the apparent activation energy for each sample are listed in Table 2. Note that

298 the observed values of the activation energies should be characterized as tentative since

299 effect of the adsorption-desorption equilibrium of the formed water would be hidden into

300 the reported value.

301   TABLE 2

302   FIGURE 3

303 The activation energy of all pure Co_3O_4 samples were very similar (71–74 kJ mol^{-1}) and

304 comparable with the values reported in the literature for this reaction [42,43]. On the other

305 hand, Figure 4 revealed that there was a good correlation between the reaction rate at

306 375 °C and the surface Co^{3+}/Co^{2+} molar ratio of the samples, which in turn was related to

307 a more active role of lattice oxygen in the reaction with respect to adsorbed species

308 [20,26,44]. The relative abundance of these catalytically active species (easily reducible

309 Co^{3+}) was optimised for the CC sample prepared by precipitation.

310   FIGURE 4

311 *3.2.   Characterisation of supported Co_3O_4/Al_2O_3 catalysts*

312 The textural properties (BET surface area, mean pore diameter and pore volume) and Co

313 loading of the supported Co_3O_4/Al_2O_3 samples (xCo/Al_2O_3) are shown in Table 3. The

314 results indicated that the cobalt species deposited over the surface of the support

315 progressively blocked its pores with increasing metallic loading, as pointed out by the

316 observed decrease in the surface area from 136 $m^2\,g^{-1}$ for the bare γ-alumina to 84 $m^2\,g^{-1}$

317 for the 40Co/Al_2O_3 catalyst. All samples presented a lower pore volume with respect to

318 the support, and this slightly decreased with Co loading. Furthermore, as can be seen in

319 Figure S3 (Supplementary material), all samples exhibited a pore size distribution centred

320 at a smaller size in comparison with the pure γ-Al_2O_3. This suggested that the addition of

321 cobalt to the alumina gradually blocked its largest pores.

322   TABLE 3

323 The XRD patterns of the alumina supported Co_3O_4 catalysts are shown in Figure 5. For

324 the sake of comparison the patterns of the bare alumina support is also included. The

325 following signals located at 2θ = 19.0°, 31.3°, 36.8°, 44.8°, 59.4° and 65.2° were clearly

326 visible. These could, in principle, be assigned to the Co_3O_4 phase. However, the presence

327 of $CoAl_2O_4$ could not be ruled out since its diffraction signals are virtually identical to

328 those of Co_3O_4. On the other hand, the signals of the support (2θ = 33.0°, 37.1°, 39.7°,

329 45.6° and 67.3°) were also observed, more noticeably in the samples with a Co loading

330 between 10 and 30%wt. On the other hand, it was clear that the crystallinity of the samples

331 increased with the Co loading since the diffraction signals became sharper. This, in turn,

332 would mean that the Co_3O_4 crystallites became larger with Co loading, but their size could

333 not be properly estimated due to the possible interference of the $CoAl_2O_4$ diffraction

334 signals. However, an attempt was made to calculate the average crystallite size of the Co-

335 phases with a spinel structure (Co_3O_4 or $CoAl_2O_4$). For this calculation the most intense

336 peak of both phases ($2\theta = 36.8°$) was not used since it overlapped with one signal

337 assignable to the γ-alumina support ($2\theta = 37.1°$). Accordingly, the signal at $2\theta = 59.4°$

338 was selected for this estimation. The calculated values evidenced that crystallite size

339 gradually increased from 13 to 35 nm with Co loading up to 35%wt. No further increase

340 was noticed for the sample with the highest metal loading (34 nm).

341   FIGURE 5

342 The structure of the samples was additionally investigated by UV-vis-NIR diffuse

343 reflectance spectroscopy. For comparative purposes two bulk cobalt aluminate samples

344 prepared by precipitation and calcined at 600 and 850 °C were used. The spectra of these

345 samples along with those corresponding to the supported catalysts are shown in Figure S4

346 (Supplementary material). For all the samples the spectra displayed three absorption

347 bands located at 1210, 1320 and 1510 nm, consistent with tetrahedral Co^{2+} species, along

348 with weak bands at 430 and 720 nm consistent with octahedral Co^{3+} species, both

349 associated with free Co_3O_4 [45,46]. In addition, a set of bands at 552, 585 and 630 nm,

350 related to the presence of $CoAl_2O_4$, was visible in the spectra of the $10Co/Al_2O_3$ and

351 $20Co/Al_2O_3$ samples [46,47]. This finding suggested that both Co_3O_4 and $CoAl_2O_4$ were

352 present in the supported catalysts. Also, the samples with a low Co content exhibited a

353 band at 1930 nm associated with hydrated alumina [48].

354 The XPS spectra of the supported samples were characterised by a lower signal/noise

355 ratio than that exhibited by bulk Co_3O_4. Hence, the deconvolution of these profiles was

356 not possible. Nevertheless, the position of the main signal of the Co 2p spectra (Figure 6)

357 could give some information about the nature of the cobalt species on the surface. The

358   binding energy of the $10Co/Al_2O_3$, $20Co/Al_2O_3$ and $30Co/Al_2O_3$ catalysts increased from

359   780.4 to 781.1−781.4 eV, thereby revealing that $CoAl_2O_4$ and Co_3O_4 coexisted on the

360   surface, in line with the results obtained by diffuse reflectance spectroscopy. Note that

361   the main signal of the Co 2p spectra in the bulk $CoAl_2O_4$ sample calcined at 600 °C is

362   located at 781.4 eV. By contrast, for the catalysts with a higher cobalt loading

363   ($35Co/Al_2O_3$ and $40Co/Al_2O_3$) the main signal (780.1−780.2 eV) was closer to that of the

364   bulk Co_3O_4 (780.1 eV). This indicated that Co_3O_4 was the most abundant phase on the

365   surface [49].

366   FIGURE 6

367   The redox properties were investigated by temperature-programmed reduction with

368   hydrogen. The resulting profiles are included in Figure 7. It is worth pointing out that all

369   cobalt species present in the catalysts were completely reduced to metallic Co. This was

370   verified by XRD analysis of the samples recovered after the TPR run since only metallic

371   Co and Al_2O_3 were detected (Figure S5, Supplementary material). Two main H_2 uptakes

372   were clearly distinguished. The first contribution, located at about 250–450 °C, could be

373   assigned to reduction of free Co_3O_4. This consumption could be in turn subdivided into

374   other two with peak reduction temperatures at 310 and 380−440 °C, following the same

375   reduction steps as for the bulk Co_3O_4 catalysts. Note that, unlike the bulk CC sample, the

376   sequential reduction $Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$ was less discernible. The second main uptake,

377   centred at higher temperatures (660–730 °C), could be related to Co species with a

378   substantially lower reducibility. In the literature there is still a debate on the nature of this

379   contribution since it could be attributed to either the formation of cobalt aluminate

380    $CoAl_2O_4$ [46,50], or to strong interactions between Co species and the alumina support

381   [26,51]. In an attempt to shed some light on the origin of this contribution, a H_2-TPR

382   analysis of the bulk cobalt aluminate calcined at 600 °C was performed in order to serve

383   as a reference for comparison with the supported catalysts. Its corresponding profile

384   included in Figure 7 was similar to those of the alumina supported catalysts. Thus, a low

385   H_2 consumption was noticed at about 450 °C, which corresponded to the reduction of

386   cobalt species (probably Co_3O_4) not fully incorporated into the lattice of $CoAl_2O_4$. Above

387   600 °C the full reduction of $CoAl_2O_4$ took place. Accordingly, the measured overall H_2

388   uptake (6.49 mmol H_2 g^{-1}) was slightly higher than the theoretical value for pure $CoAl_2O_4$

389   (5.65 mmol H_2 g^{-1}). Therefore, the comparison between the profiles of the alumina

390   supported catalysts and that of the bulk $CoAl_2O_4$ sample evidenced that the high-

391   temperature H_2 consumption observed on the supported Co_3O_4 samples could be assigned

392   to the presence of varying amounts of cobalt aluminate. Note that the shoulder at about

393   900 ºC observed in the profile of the $20Co/Al_2O_3$ catalyst was due to an instrumental

394   artifact involving the application of the heating ramp of the experiment. Occasionally,

395   when the temperature were close (about 10 °C lower) to the temperature limit of the run

396   (in this case, 900 ºC), the furnace would stop heating. Then the ongoing reduction process

397   underwent a sudden halt that resulted in that small sharp peak, which had no meaning on

398   the redox properties of the sample.

399   The quantitative integration of the profiles (Table 3) revealed that the overall H_2 uptake

400   of the $10Co/Al_2O_3$ and $20Co/Al_2O_3$ catalysts was very close to that expected when

401   assuming that all cobalt species were present as $CoAl_2O_4$. By contrast, the observed

402   uptake for the $35Co/Al_2O_3$ and $40Co/Al_2O_3$ samples was comparable with that

403   theoretically predicted for the exclusive presence of Co_3O_4. Based on the corresponding

404   H_2 consumption at 250–450 °C and 600–800 °C the relative distribution of Co species

405   between Co_3O_4 and $CoAl_2O_4$ could be estimated for each sample. It was found that cobalt

406   aluminate was the principal phase over the catalyst with the lowest loading ($10Co/Al_2O_3$).

407   When increasing the metal content up to 20wt% the amount of both species increased. It

408   therefore seemed that the previously formed $CoAl_2O_4$ layer grew. However, above this

409   Co concentration ($30Co/Al_2O_3$, $35Co/Al_2O_3$ and $40Co/Al_2O_3$ samples) the amount of

410   metal as $CoAl_2O_4$ remained constant around 13-14wt.%, irrespective of the cobalt

411   loading. It could be then reasonably believed that the formed Co_3O_4 crystallites were

412   located on top of this aluminate layer, and in principle, did not further converted into

413   aluminate. This assumption was coherent with the larger H_2 uptake required for the

414   reduction of free Co_3O_4 over these samples.

415   FIGURE 7

416

417   *3.3.   Characterisation of Ce-doped Co_3O_4 bulk catalysts*

418   The textural and structural properties of the bulk Ce-doped Co_3O_4 (xCe/Co_3O_4) samples

419   along with the CC sample and pure CeO_2 (for reference) are shown in Table 4. The

420   specific surface area of Ce-doped catalysts varied between 30 and 35 m^2 g^{-1}, which was

421   more than twice that of the surface area of the CC sample, while the pore volume

422   increased by 50% approximately and the pore diameter decreased by the same amount,

423   thus demonstrating that the addition of Ce to the bulk Co_3O_4 could improve their textural

424   properties.

425   TABLE 4

426   The xCe/Co_3O_4 samples showed the various diffraction signals of the cubic Co_3O_4 but

427   slightly shifted from their positions with respect to the pure spinel (Figure 8). In addition,

428   the crystallite size significantly decreased from 63 to 29−38 nm. On the other hand, the

429   samples with a Ce loading of 15 and 20wt% also exhibited signals ($2\theta = 28.8°$, $33.3°$,

430   $47.7°$, $56.6°$, $59.4°$, $69.6°$, $76.9°$ and $79.3°$) related to segregated cubic fluorite-like CeO_2

431   (JCPDS 00-034-0394). These evidences pointed out that the addition of Ce caused a

432   distortion in the spinel structure, which in turn decreased the Co_3O_4 crystallite size and

433   increased the unit cell size, but only for the Ce loadings of 5 and 10%wt., as can be seen

434   in Figure S6 (Supplementary material). These effects have also been reported by other

435   authors [52,53], with the latter being attributed to the larger ionic radius of Ce^{4+} (101 pm)

436   in comparison with Co^{2+} (79 pm) and Co^{3+} (69 pm). The upper limit for the amount of

437   cerium atoms that could be inserted into the lattice of Co_3O_4 seemed to be close to 10%wt.

438   Above this loading, excess of cerium led to the formation of segregated CeO_2.

439   FIGURE 8

440   To further assess the distortion caused by the insertion of Ce atoms into the lattice of the

441   Co_3O_4 spinel, Raman spectrometry was applied to all Ce-doped samples. The resulting

442   spectra are included in Figure 9. The doped oxides displayed the same five Raman bands

443   also observed for the pure Co_3O_4, but shifted from their original positions and with

444   broader shapes, thus suggesting the distortion of the Co_3O_4 lattice. Hence, the bands

445   located at 194, 519 and 617 cm^{-1} could be assigned to the F_{2g} mode, while the bands at

446   479 and 687 cm^{-1} could be assigned to the E_g and A_{1g} modes, respectively [13]. Pure

447   CeO_2, however, only displayed a markedly intense signal, located at 462 cm^{-1}, attributable

448   to the symmetrical stretching of CeO_8 units [54]. The xCe/Co_3O_4 samples also exhibited

449   much weaker forms of this signal, also shifted from its original position. This pointed out

450   that the segregated CeO_2 in the $15Ce/Co_3O_4$ and $20Ce/Co_3O_4$ samples could also present

451   some degree of distortion on its own lattice. The band related to the A_{1g} mode showed a

452   much broader shape for the Ce-doped samples, with relatively higher FWHM values

453   between 17 and 27 cm^{-1} in comparison with the pure cobalt oxide (11 cm^{-1}). The highest

454   values were noted over the samples $5Ce/Co_3O_4$ and $10Ce/Co_3O_4$, thereby pointing out that

455   the largest extent of lattice distortion occurred in these catalysts. Accordingly, these were

456   the samples that presented the largest cell size.

457   FIGURE 9

458   The XPS analysis of Ce-doped samples also helped in determining the role of Ce and its

459   eventual influence on the valence changes of cobalt species. The spectra of all xCe/Co_3O_4

460   samples were fitted with ten peaks corresponding to five pairs of spin-orbit doublets.

461   Following the convention adopted by Romeo et al. [55], letters U and V were used to

462   refer to the $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components, respectively. From the five pairs of

463   peaks, three of them (namely V,U; V'',U'' and V''',U''') were associated with electrons

464   from Ce^{4+} while the remaining pairs (V_0,U_0 and V',U') were attributed to electrons from

465   Ce^{3+} species. As an example, the fitted Ce3d spectrum of the $10Ce/Co_3O_4$ sample is

466   shown in Figure S7 (Supplementary material).

467   The Ce^{3+}/Ce^{4+} molar ratios were obtained from the areas of both $3d_{5/2}$ and $3d_{3/2}$

468   components for each species. These calculated ratios were correlated with the molar

469   Co^{3+}/Co^{2+} ratios calculated from the respective Co2p spectra, as shown in Figure 10. An

470   inverse relationship was found, which could be explained in terms of the equilibrium Ce^{3+}

471     $+ Co^{3+} \leftrightarrow Ce^{4+} + Co^{2+}$, established by the requirement of charge balance within the cations

472   of the spinel lattice [56,57]. An increase in Co^{3+} population at the cost of Co^{2+} resulted in

473   a decrease of Ce^{3+} ions in favour of Ce^{4+}.

474   FIGURE 10

475   The redox properties of the Ce-doped catalysts were investigated by temperature-

476   programmed reduction with hydrogen (H_2-TPR) and temperature-programmed reaction

477   with methane (CH_4-TPRe). The corresponding H_2-TPR profiles are included in Figure 11.

478   The hydrogen consumption profiles of the xCe/Co_3O_4 catalysts were similar to those

479   displayed by the bulk CC Co_3O_4, showing the same two-step reduction process, with peak

480   temperatures at 310 and 375 °C. Note that the second reduction peak, assigned to the

481   reduction of Co^{2+} ions, was characterised by a broader temperature window with respect

482   to the pure cobalt oxide, probably due to the distortion caused by the insertion of Ce atoms

483   into the spinel lattice. The reduction profile of CeO_2 also exhibited a two-step reduction

484   process, where the first step, centred at about 320 °C, is usually attributed to the reduction

485   of the surface while the second one, located at 735 °C, is assigned to the reduction of the

486   bulk [58]. However, the intensity of these reduction events was substantially lower than

487   for the reduction of Co_3O_4, and none of the Ce-doped catalysts revealed signals of CeO_2

488   reduction in their TPR profiles, presumably owing to the low amount of free CeO_2 present

489   in the samples. The results included in Table 5 pointed out that Ce doping did not result

490   in a relevant variation of the relative H_2 uptake at low and high temperature corresponding

491   to the reduction of the spinel.

492   FIGURE 11

493   TABLE 5

494   Since the investigation of the redox properties of the xCe/Co_3O_4 oxides by H_2-TPR did

495   not evidence marked differences among the various samples, a new attempt was made by

496   substituting H_2 by CH_4. This change could provide more useful insights on the

497   characterisation and identification of the available oxygen species for methane oxidation.

498   The exit stream of the CH_4-TPRe experiment was analysed by mass spectrometry. Thus,

499   the $m/z = 44$ (CO_2) and the $m/z = 28$ (CO) signals were monitored. The evolution of these

500   two species with the temperature for all xCe/Co_3O_4 catalysts and the CC sample are

501   shown in Figure 12.

502   FIGURE 12

503   Over all samples the formation of CO_2 occurred at 350–550 ºC and 600–700 ºC. At lower

504   temperatures the generation was assigned to the oxidation of methane by oxygen species

505   associated with Co^{3+} ions. At higher temperatures the CO_2 production was attributed to

506   the oxidation of methane by oxygen species associated with Co^{2+} ions [59]. However, as

507   opposed to the H_2-TPR profiles, the temperature windows for both reactions were clearly

508 discernible. In all cases, the formation of CO_2 at high temperatures was also accompanied

509 by the generation of CO and H_2 to some extent. This could be due to the ability of Co^{2+}

510 ions to catalyse the reforming of methane as well [60] and also due to the deficit of oxygen

511 present in the catalysts after all Co^{3+} ions were reduced. Both CO_2 contributions took the

512 shape of definite non-Gaussian peaks. Interestingly, for the $10Ce/Co_3O_4$ sample, the

513 formation of CO_2 occurred at significantly lower temperatures (460 and 605 °C) when

514 compared with the CC sample (485 and 620 °C). Each CH_4-TPRe experiment was

515 followed by a H_2-TPR analysis to check if methane could completely reduce the catalysts.

516 No hydrogen uptake was found, thereby evidencing that all samples were completely

517 reduced by methane. Integration and quantification of the CO_2 production at low and high

518 temperatures (Table 5) revealed a better behaviour for the conversion of CH_4 at low

519 temperatures over the $10Ce/Co_3O_4$ sample. These results demonstrated that the addition

520 of small amounts of Ce to bulk Co_3O_4 catalysts improved their ability for methane

521 oxidation.

522

523 *3.4.   Comparison between Co_3O_4/Al_2O_3 and Ce-doped Co_3O_4 bulk catalysts*

524 Catalytic activity of alumina supported and Ce-doped Co_3O_4 catalysts were examined

525 under the same conditions as for the bulk Co_3O_4 catalysts. The corresponding light-off

526 curves are included in Figure 13. It was noticed that the activity of the alumina supported

527 samples expectedly increased with Co loading, with a T_{50} value of 515 and 510 °C over

528 the $35Co/Al_2O_3$ and $40Co/Al_2O_3$ catalysts, respectively. Nevertheless, in no case their

529 activity was higher than that of the bulk catalysts, despite exhibiting much better textural

530 properties. This was probably due to two reasons. First, cobalt aluminate, hardly reducible

531 at the selected reaction temperatures, fixed a great amount of the cobalt deposited, thereby

532 decreasing the availability of potentially active cobalt species. Recall that the activity of

533   pure $CoAl_2O_4$ was negligible. Secondly, as shown by the H_2-TPR profiles, the amount of

534   easily reducible, highly active Co^{3+} in the supported catalysts was lower than that of bulk

535   catalysts, which made free Co_3O_4 within the support less active than the bulk Co_3O_4.

536   Similar results were obtained by other authors, for Co_3O_4/Al_2O_3 catalysts obtained by

537   both wet [11] and incipient wetness impregnation [26].

538   FIGURE 13

539   The reaction rate estimated under differential conditions (X<20% at 425 ℃) are listed in

540   Table 2. The highest reaction rate was found over the $35Co/Al_2O_3$ catalyst (2.2 mmol CH_4

541   g_{Co}^{-1} h^{-1}) followed by the $40Co/Al_2O_3$ and $30Co/Al_2O_3$ samples (2.1 and 1.9 mmol CH_4

542   g_{Co}^{-1} h^{-1}, respectively). By contrast, both $10Co/Al_2O_3$ and $20Co/Al_2O_3$ samples showed a

543   noticeably lower reaction rate, around 1.2 mmol CH_4 g_{Co}^{-1} h^{-1}. On the other hand, a

544   progressive decrease in the apparent activation energy with Co loading was evident. Over

545   the catalysts with a low Co content, where $CoAl_2O_4$ was the most abundant phase, the

546   activation energy was around 100 kJ mol^{-1}. For higher loadings, and more particularly

547   over the $35Co/Al_2O_3$ and $40Co/Al_2O_3$ catalysts, the activation energy was close (78−79

548   kJ mol^{-1}) to that observed for the bulk Co_3O_4 catalyst (CC sample). These values were

549   evaluated from the fit of experimental conversion data to the Equation 1.

550   Regarding Ce-doped samples all the light-off curves were relatively similar with a T_{50} in

551   the 425−435 °C range. It must be pointed out that the pure CeO_2 was virtually inactive,

552   with a conversion as low as 10% at 600 °C. Only the $10Ce/Co_3O_4$ sample showed a

553   slightly better behaviour with respect to the pure bulk Co_3O_4 catalyst. More perceptible

554   differences were noticed when the specific reaction rates at 375 °C (X<20%) were

555   compared. Thus, it was 2 mmol CH_4 g_{Co}^{-1} h^{-1} over the $10Ce/Co_3O_4$ sample and 1.8 mmol

556   CH_4 g_{Co}^{-1} h^{-1} over the pure cobalt oxide. This revealed that the addition of cerium had a

557   positive effect on the specific activity of bulk Co_3O_4. It is worth pointing out that the

558   alumina supported catalysts required temperatures at least 50 °C higher to achieve similar

559   reaction rates. The estimated apparent activation energy of the $5Ce/Co_3O_4$, $10Ce/Co_3O_4$

560   and $15Ce/Co_3O_4$ catalysts were 78–79 kJ mol^{-1}, close to the value determined for the pure

561   counterpart. Over the $20Ce/Co_3O_4$ catalyst, characterised by a considerable amount of

562   segregated ceria, the value significantly increased up to 85 kJ mol^{-1}. Note that pure CeO_2

563   gave an activation energy of 108 kJ mol^{-1}. The relationship shown in Figure 14 revealed

564   that the specific reaction rate was clearly influenced by the mobility of the oxygen species,

565   which was evaluated from the amount of oxygen reacting with methane at low

566   temperatures, which corresponded to the $Co^{3+} \rightarrow Co^{2+}$ reduction step in the CH_4-TPRe

567   run. In sum, it could be concluded that the addition of small amounts of cerium atoms,

568   which were introduced into the lattice of Co_3O_4, resulted in an enhancement of the

569   intrinsic activity of the spinel owing to a distortion of the crystalline structure which

570   ultimately led to an increased population of Co^{3+}, an improved reducibility and a higher

571   mobility of the oxygen species in the spinel lattice.

572   FIGURE 14

573   The deep oxidation of methane over Ce-Co oxide catalysts has been widely investigated

574   in the recent years. For example, Li et al. achieved a T_{50} of 400 °C (25 °C lower than in

575   this work) under similar reaction conditions over a Ce-Co catalyst prepared by a sol-gel

576   method [28]. Vickers et al. obtained comparable results (T_{50} around 400 °C) using CeO_2

577   supported over a meso-Co_3O_4 obtained using KIT-6 as hard template but operating at

578   180 mL CH_4 g^{-1} h^{-1} [61]. In both cases, the Ce/Co molar ratio (0.33 and 0.10, respectively)

579   used was significantly higher than in this work (0.06), which points out that the activity

580   promoting effect of cerium in those catalysts was actually lower than that observed in this

581   work. In addition, Liotta et al. [62] achieved a T_{50} of 455 °C (180 mL CH_4 g^{-1} h^{-1}) by

582   using Co_3O_4 supported over CeO_2 with a Ce/Co molar ratio of 1.1. Our results therefore

583 evidenced that active Ce-Co catalysts could be designed with a relatively low Ce content.

584 Finally, attention was also paid to examining the stability of the most active catalysts,

585 namely $10Ce/Co_3O_4$ and CC samples, when operating at constant temperature (450 °C)

586 during a relatively prolonged time (150 hours). The results included in Figure S8

587 (Supplementary material) revealed that both oxides gave a relatively stable conversion

588 close to 75%, although the cerium-free sample showed a slight instability. The

589 characterisation of the used $10Ce/Co_3O_4$ sample by BET measurements and XRD

590 revealed a reduced impact on its surface area (30 m^2 g^{-1}, 35 m^2 g^{-1} for the fresh sample)

591 and crystallite size (30 nm, 29 nm for the fresh sample).

592 Given the reasonably good results achieved by the $10Ce/Co_3O_4$ catalyst its stability at

593 425 ºC was also evaluated under humid conditions (in the presence of 5% H_2O) for 150

594 hours. The results are also shown in Figure S8 (Supplementary material). It was found

595 that water noticeably decreased the catalytic performance with a reasonably constant

596 conversion around 40%. The surface area after this run decreased to 24 m^2 g^{-1} in line with

597 the concomitant enlargement of the crystallite size (35 nm). This used sample was further

598 submitted to an additional stability test under dry conditions for 20 hours (Figure S8,

599 Supplementary material). It was noticed that conversion was not fully recovered, but it

600 was still around 65%. This finding certainly evidenced that water, apart from inhibiting

601 the catalytic activity by competitive effects, also had a significant negative effect on the

602 physicochemical properties of the sample [17,63].

603

604 **4. Conclusions**

605 The performance of three type of Co_3O_4 catalysts, namely bulk, alumina-supported and

606 Ce-doped samples, was examined for the combustion of methane under similar reaction

607 conditions to those in the exhaust gas of VNG engines. The activity of bulk catalysts was

608 found to be controlled by an increased Co^{3+}/Co^{2+} molar ratio that in turn evidenced a more

609 active role of surface lattice oxygen in the reaction. Higher reaction rates were achieved

610 by Co_3O_4 catalysts prepared by basic aqueous precipitation. Interestingly, the addition of

611 a relatively small amount of cerium (10%wt.) to the Co_3O_4 lattice led to an increase in

612 the inherent catalytic activity of the cobalt phase due to an improvement in the mobility

613 of lattice oxygen species associated with easily reducible Co^{3+} ions. This optimised

614 catalyst exhibited a marked stability under both dry and humid conditions during a

615 relatively prolonged reaction time. On the other hand, owing to the notable negative

616 impact induced by cobalt aluminate formation, the behaviour of alumina supported

617 catalysts was shown to be inferior with respect to the bulk samples. As a result, notable

618 conversion levels were only attained with a Co loading higher than 30%wt.

619

625

626 **Appendix A. Supplementary data**

627 Supplementary data associated with this article can be found in the online version.

628

629 **References**

630 [1] M.I. Jahirul, H.H. Masjuki, R. Saidur, M.A. Kalam, M.H. Jayed, M.A. Wazed,
631   Appl. Therm. Eng. 30 (2010) 2219-2226.

632 [2] M. Hussain, F.A. Deorsola, N. Russo, D. Fino, R. Pirone, Fuel 149 (2015) 2-7.

633 [3] S. Di Pascoli, A. Femia, T. Luzzati, Ecol. Econ. 38 (2001) 179-189.

634 [4]   T. Korakianitis, A.M. Namasivayam, R.J. Crookes, Prog. Energ. Combust. 37
635   (2011) 89-112.

636 [5]   Z. Li, G.B. Hoflund, J. Nat. Gas Chem. 12 (2003) 153-160.

637 [6]   J.K. Lampert, M.S. Kazi, R.J. Farrauto, Appl. Catal. B Environ. 14 (1997) 211-
638   223.

639 [7]   Q. Xu, K.C. Kharas, B.J. Croley, A.K. Datye, ChemCatChem 3 (2011) 1004-
640   1014.

641 [8]   L.S. Escandón, D. Niño, E. Díaz, S. Ordóñez, F.V. Díez, Catal. Commun. 9 (2008)
642   2291-2296.

643 [9]   S. Ordóñez, J.R. Paredes, F.V. Díez, Appl. Catal. A Gen. 341 (2008) 174-180.

644 [10] A. Setiawan, E.M. Kennedy, B.Z. Dlugogorski, A.A. Adesina, M. Stockenhuber,
645   Catal. Today 258 (2015) 276-283.

646 [11] T. Xiao, S. Ji, H. Wang, K.S. Coleman, M.L.H. Green, J. Mol. Catal. A Chem.
647   175 (2001) 111-123.

648 [12] J. Chen, H. Arandiyan, X. Gao, J. Li, Catal. Surv. Asia 19 (2015) 140-171.

649 [13] Q. Liu, L. Wang, M. Chen, Y. Cao, H. He, K. Fan, J. Catal. 263 (2009) 104-113.

650 [14] G. Salek, P. Alphonse, P. Dufour, S. Guillemet-Fritsch, C. Tenailleau, Appl.
651   Catal. B Environ. 147 (2014) 1-7.

652 [15] Q. Ren, S. Mo, R. Peng, Z. Feng, M. Zhang, L. Chen, M. Fu, J. Wu, D. Ye, J.
653   Mater. Chem. A 6 (2018) 498-509.

654 [16] J. González-Prior, R. López-Fonseca, J.I. Gutiérrez-Ortiz, B. de Rivas, Appl.
655   Catal. B Environ. 222 (2018) 9-17.

656 [17] L.F. Liotta, G. Di Carlo, G. Pantaleo, A.M. Venezia, G. Deganello, Appl. Catal.
657   B Environ. 66 (2006) 217-227.

658 [18] N. Bahlawane, Appl. Catal. B Environ. 67 (2006) 168-176.

659 [19] Y. Ji, Z. Zhao, A. Duan, G. Jiang, J. Liu, J. Phys. Chem. C 113 (2009) 7186-7199.

660 [20] N. Bahlawane, P.H.T. Ngamou, V. Vannier, T. Kottke, J. Heberle, K. Kohse-
661   Höinghaus, Phys. Chem. Chem. Phys. 11 (2009) 9224-9232.

662 [21] Z. Tian, P.H. Tchoua Ngamou, V. Vannier, K. Kohse-Höinghaus, N. Bahlawane,
663   Appl. Catal. B Environ. 117-118 (2012) 125-134.

664 [22] N. van Vegten, T. Baidya, F. Krumeich, W. Kleist, A. Baiker, Appl. Catal. B
665   Environ. 97 (2010) 398-406.

666   [23]   Z. Chen, S. Wang, W. Liu, X. Gao, D. Gao, M. Wang, S. Wang, Appl. Catal. A
667   Gen. 525 (2016) 94-102.

668   [24]   Z. Pu, H. Zhou, Y. Zheng, W. Huang, X. Li, Appl. Surf. Sci. 410 (2017) 14-21.

669   [25]   U. Zavyalova, P. Scholz, B. Ondruschka, Appl. Catal. A Gen. 323 (2007) 226-
670   233.

671   [26]   Q. Wang, Y. Peng, J. Fu, G.Z. Kyzas, S.M.R. Billah, S. An, Appl. Catal. B
672   Environ. 168-169 (2015) 42-50.

673   [27]   N.E. Machin, C. Karakaya, A. Celepci, Energ. Fuel. 22 (2008) 2166-2171.

674   [28]   H. Li, G. Lu, D. Qiao, Y. Wang, Y. Guo, Y. Guo, Catal. Lett. 141 (2011) 452-
675   458.

676   [29]   M. Kumar, G. Rattan, R. Prasad, Can. Chem. Trans. 3 (2015) 381-409.

677   [30]   B. De Rivas, R. López-Fonseca, C. Jiménez-González, J.I. Gutiérrez-Ortiz, J.
678   Catal. 281 (2011) 88-97.

679   [31]   A.A. Mirzaei, H.R. Shaterian, R.W. Joyner, M. Stockenhuber, S.H. Taylor, G.J.
680   Hutchings, Catal. Commun. 4 (2003) 17-20.

681   [32]   Eurokin. http://eurokin.org/, 2018 (accessed 20 February 2018).

682   [33]   A. Aranzabal, J.A. González-Marcos, J.L. Ayastuy, J.R. González-Velasco,
683   Chem. Eng. Sci. 61 (2006) 3564-3576.

684   [34]   C. Shi, Y. Wang, A. Zhu, B. Chen, C. Au, Catal. Commun. 28 (2012) 18-22.

685   [35]   A. Biabani-Ravandi, M. Rezaei, Chem. Eng. J. 184 (2012) 141-146.

686   [36]   S. Arnone, G. Bagnasco, G. Busca, L. Lisi, G. Russo, M. Turco, Stud. Surf. Sci.
687   Catal. 119 (1998) 65-70.

688   [37]   J. González-Prior, R. López-Fonseca, J.I. Gutiérrez-Ortiz, B. de Rivas, Appl.
689   Catal. B Environ. 199 (2016) 384-393.

690   [38]   S.A. Singh, G. Madras, Appl. Catal. A Gen. 504 (2015) 463-475.

691   [39]   M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C.
692   Smart, Appl. Surf. Sci. 257 (2011) 2717-2730.

693   [40]   J. Dupin, D. Gonbeau, P. Vinatier, A. Levasseur, Phys. Chem. Chem. Phys. 2
694   (2000) 1319-1324.

695   [41]   P. Stefanov, S. Todorova, A. Naydenov, B. Tzaneva, H. Kolev, G. Atanasova, D.
696   Stoyanova, Y. Karakirova, K. Aleksieva, Chem. Eng. J. 266 (2015) 329-338.

697   [42]   G.I. Golodets, Chapter V: The Kinetics of Gas-Phase Heterogeneous Catalytic
698   Reactions Involving Molecular Oxygen, in: G.I. Golodets (Ed.), Heterogeneous
699   Catalytic Reactions Involving Molecular Oxygen, Elsevier, Amsterdam, 1983, pp.
700   126-150.

701   [43]   J.R. Paredes, E. Díaz, F.V. Díez, S. Ordónez, Energ. Fuel. 23 (2009) 86-93.

702   [44]   J. Li, X. Liang, S. Xu, J. Hao, Appl. Catal. B Environ. 90 (2009) 307-312.

703   [45]   Y. Brik, M. Kacimi, M. Ziyad, F. Bozon-Verduraz, J. Catal. 202 (2001) 118-128.

704   [46]   L.G.A. van de Water, G.L. Bezemer, J.A. Bergwerff, M. Versluijs-Helder, B.M.
705   Weckhuysen, K.P. de Jong, J. Catal. 242 (2006) 287-298.

706   [47]   T. Das, S. Sengupta, G. Deo, React. Kinet. Mech. Catal. 110 (2013) 147-162.

707   [48]   F. Dumond, E. Marceau, M. Che, J. Phys. Chem. C 111 (2007) 4780-4789.

708   [49]   X. Duan, M. Pan, F. Yu, D. Yuan, J. Alloy. Compd. 509 (2011) 1079-1083.

709   [50]   I. Zacharaki, C.G. Kontoyannis, S. Boghosian, A. Lycourghiotis, C. Kordulis,
710   Catal. Today 143 (2009) 38-44.

711   [51]   B. Solsona, T.E. Davies, T. Garcia, I. Vázquez, A. Dejoz, S.H. Taylor, Appl.
712   Catal. B Environ. 84 (2008) 176-184.

713   [52]   D. Li, L. Wang, M. Koike, Y. Nakagawa, K. Tomishige, Appl. Catal. B Environ.
714   102 (2011) 528-538.

715   [53]   G. Zou, Y. Xu, S. Wang, M. Chen, W. Shangguan, Catal. Sci. Technolog. 5 (2015)
716   1084-1092.

717   [54]   K.K. Babitha, A. Sreedevi, K.P. Priyanka, B. Sabu, T. Varghese, Indian J. Pure
718   Appl. Phys. 53 (2015) 596-603.

719   [55]   M. Romeo, K. Bak, J. El Fallah, F. Le Normand, L. Hilaire, Surf. Interface Anal.
720   20 (1993) 508-512.

721   [56]   J. Chen, C. Li, S. Li, P. Lu, L. Gao, X. Du, Y. Yi, Chem. Eng. J. 338 (2018) 358-
722   368.

723   [57]   R. Dziembaj, A. Chojnacka, Z. Piwowarska, M. Gajewska, M. Swietoslawski, S.
724   Górecka, M. Molenda, Catal Today (2018) 'in press'.

725   [58]   M. Florea, F. Matei-Rutkovska, G. Postole, A. Urda, F. Neatu, V.I. Pârvulescu, P.
726   Gelin, Catal. Today 306 (2018) 166-171.

727   [59]   L. Hu, Q. Peng, Y. Li, J. Am. Chem. Soc. 130 (2008) 16136-16137.

728 [60] A.W. Budiman, S. Song, T. Chang, C. Shin, M. Choi, Catal. Surv. Asia 16 (2012)
729   183-197.

730 [61] S.M. Vickers, R. Gholami, K.J. Smith, M.J. MacLachlan, ACS Appl. Mater. Inter.
731   7 (2015) 11460-11466.

732 [62] L.F. Liotta, G. Di Carlo, G. Pantaleo, G. Deganello, Appl. Catal. B Environ. 70
733   (2007) 314-322.

734 [63] D. Qiao, G. Lu, Y. Guo, Y. Wang, Y. Guo, J. Rare Earth. 28 (2010) 742-746.

735

Catalyst	S_{BET}, $m^2\,g^{-1}$	V_p, $cm^3\,g^{-1}$	D_p, Å	$D_{Co_3O_4}$, nm	Low-temperature H_2 uptake, mmol g^{-1}	High-temperature H_2 uptake, mmol g^{-1}	Relative H_2 uptake at low and high temperature	Co^{3+}/Co^{2+} (XPS)	O_{ads}/O_{latt} (XPS)
CC	14	0.09	257	63	4.3	12.4	0.35	1.96	0.40
HC	12	0.06	350	64	4.0	12.3	0.33	1.70	0.49
DC	5	0.02	353	84	3.9	12.8	0.30	1.50	0.57
COM	8	0.03	412	75	4.1	12.3	0.33	1.76	0.49

761

762   Table 1

Catalyst	T_{10}, °C	T_{50}, °C	T_{90}, °C	Reaction rate, mmol CH$_4$ g$_{Co}^{-1}$ h^{-1}	E_a, kJ mol^{-1}
CC	335	430	505	1.85[a]	74
HC	355	455	540	1.46[a]	74
DC	365	480	575	1.07[a]	74
COM	350	440	520	1.70[a]	71
10Co/Al$_2$O$_3$	510	>600	>600	1.17[b]	100
20Co/Al$_2$O$_3$	485	580	>600	1.17[b]	92
30Co/Al$_2$O$_3$	440	550	>600	1.87[b]	80
35Co/Al$_2$O$_3$	410	515	575	2.23[b]	78
40Co/Al$_2$O$_3$	350	440	520	2.12[b]	79
CeO$_2$	>600	>600	>600	---	108
5Ce/Co$_3$O$_4$	340	435	515	1.81[a]	78
10Ce/Co$_3$O$_4$	340	425	495	2.04[a]	79
15Ce/Co$_3$O$_4$	340	435	500	1.97[a]	79
20Ce/Co$_3$O$_4$	350	435	495	1.90[a]	85

[a]Reaction rate calculated at 375 °C under differential conditions, methane conversion was below 20% over this set of Co$_3$O$_4$-based catalysts.
[b]Reaction rate calculated at 425 °C under differential conditions, methane conversion was below 20% over this set of Co$_3$O$_4$-based catalysts.

Table 2

Catalyst	% Co	S_{BET}, $m^2 g^{-1}$	V_p, $cm^3 g^{-1}$	D_p, Å	$D_{Co\text{-}phase}$, nm	Low-temperature H_2 uptake, mmol g^{-1}	High-temperature H_2 uptake, mmol g^{-1}	% Co as Co_3O_4	%Co as $CoAl_2O_4$
γ-Al_2O_3	-	136	0.55	123	-	-	-	-	-
$10Co/Al_2O_3$	9.0	138	0.32	74	13	0.23	1.37	1.0	8.0
$20Co/Al_2O_3$	21.7	120	0.34	94	16	1.75	2.35	7.7	14.0
$30Co/Al_2O_3$	27.9	108	0.29	89	29	3.11	2.40	13.7	14.2
$35Co/Al_2O_3$	33.1	95	0.23	82	35	4.62	2.28	20.0	13.1
$40Co/Al_2O_3$	40.5	84	0.23	90	34	6.36	2.37	27.0	13.5

769

770   Table 3

Catalyst	S_{BET}, $m^2 \, g^{-1}$	V_p, $cm^3 \, g^{-1}$	D_p, Å	$D_{Co_3O_4}$, nm	Ce/Co molar ratio	Co_3O_4 cell size, Å
CC	14	0.09	257	63	0	8.0958
$5Ce/Co_3O_4$	33	0.14	155	32	0.033 (0.030)	8.0980
$10Ce/Co_3O_4$	35	0.14	143	29	0.063 (0.064)	8.0982
$15Ce/Co_3O_4$	30	0.11	176	38	0.100 (0.101)	8.0948
$20Ce/Co_3O_4$	34	0.11	153	35	0.142 (0.143)	8.0940
CeO_2	12	0.05	235	-	-	-

771   Values in brackets correspond to the nominal Ce/Co molar ratios

772   Table 4

Catalyst	H₂-TPR			CH₄-TPRe		
	Low-temperature peak, mmol g^{-1}	High-temperature peak, mmol g^{-1}	Relative H_2 uptake at low and high temperature	Low-temperature peak, °C	High-temperature peak, °C	Relative CO_2 production at low and high temperature
CC	4.29	12.41	0.35	485	620	0.56
5Ce/Co₃O₄	3.80	11.38	0.33	480	680	0.54
10Ce/Co₃O₄	3.76	10.36	0.36	460	605	0.66
15Ce/Co₃O₄	3.42	9.68	0.35	500	675	0.61
20Ce/Co₃O₄	3.15	9.20	0.34	510	695	0.63

773

774   Table 5

Figure 1

775

776

777

778

Figure 2

779

780

781

Figure 3

783

784

Figure 4

785

786

787

Figure 5

788

789

Figure 6

793

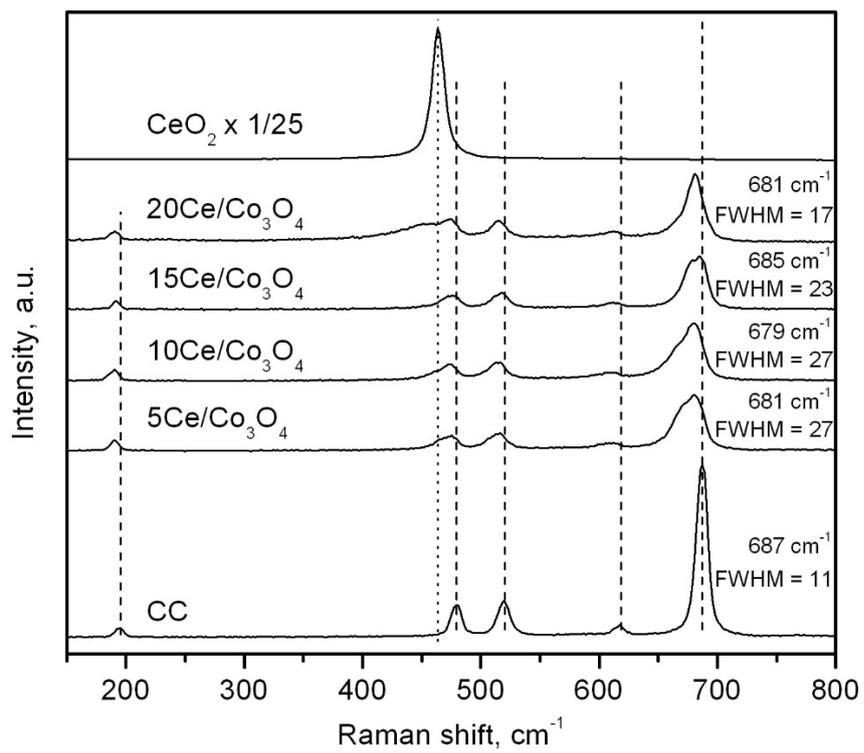794   Figure 7

795

Figure 8

796

797

798

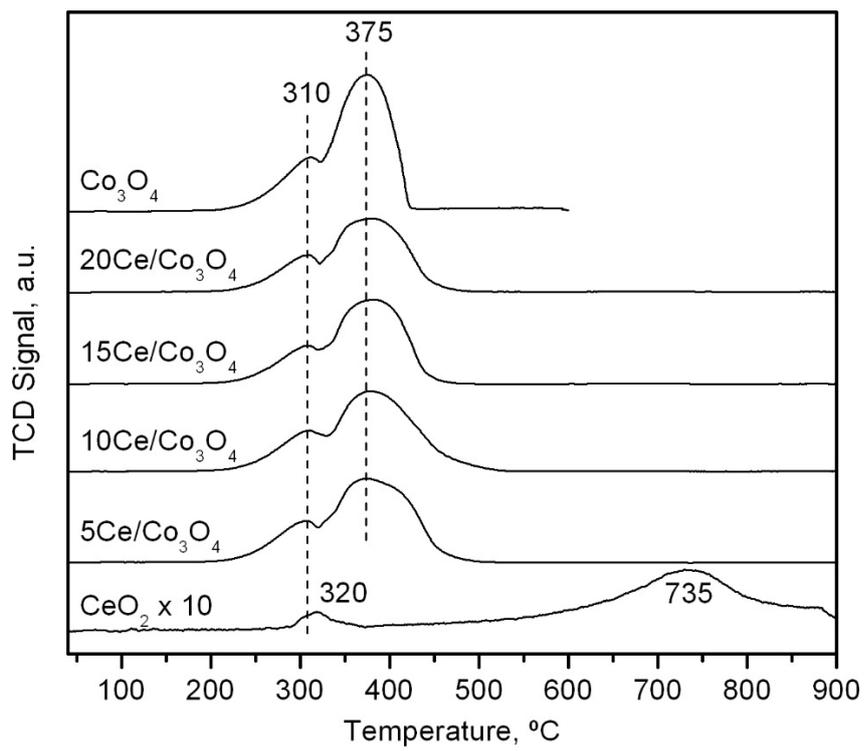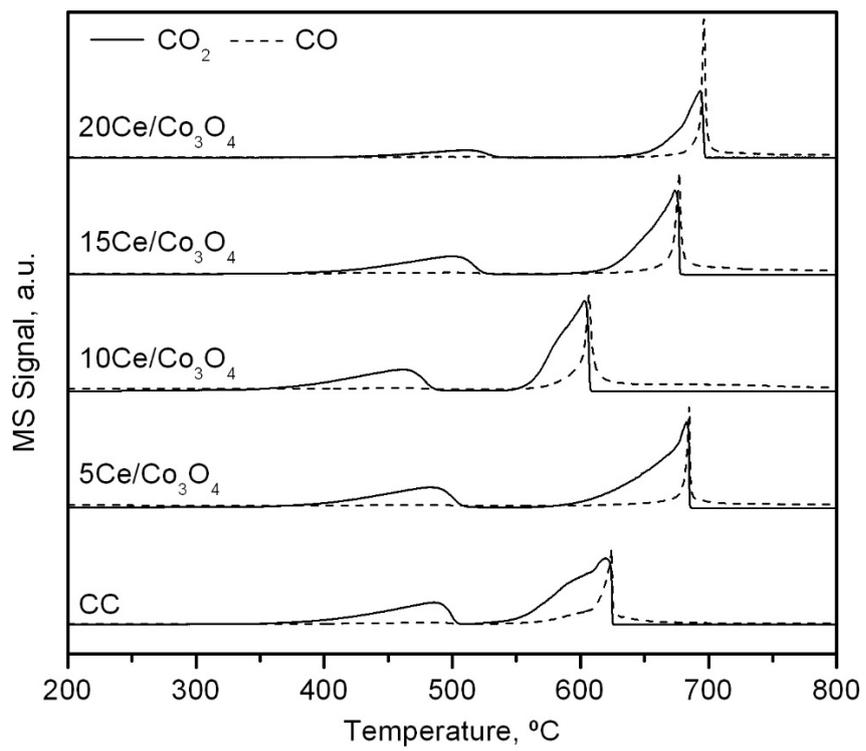Figure 9

799

800

801

802

Figure 10

803

804

Figure 11

805

806

807

808

Figure 12

809

810

811

Figure 13

812

813
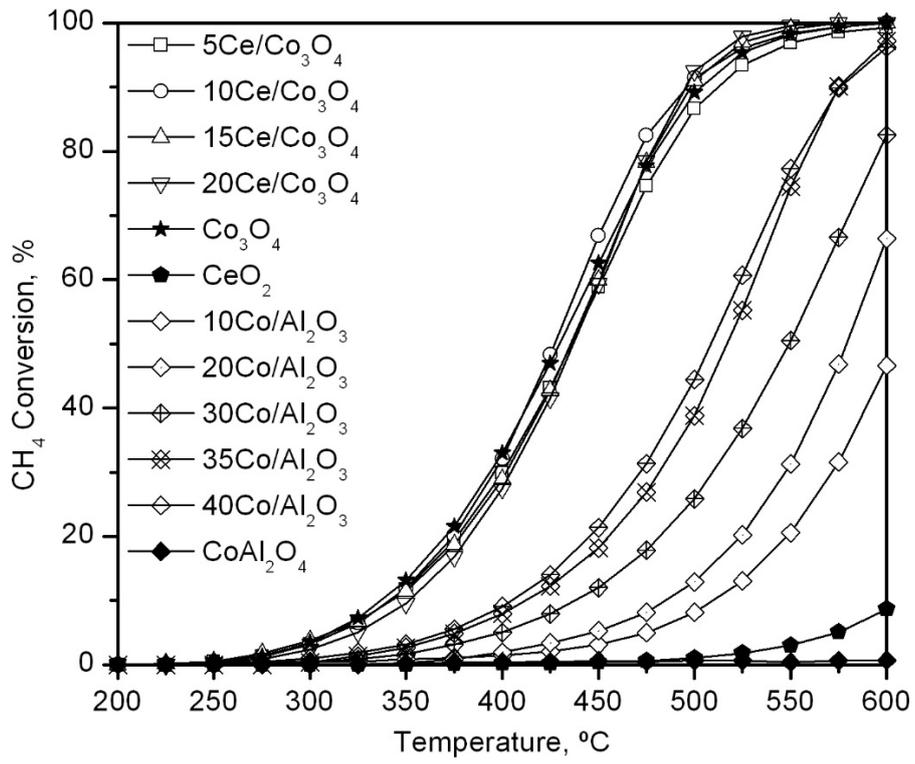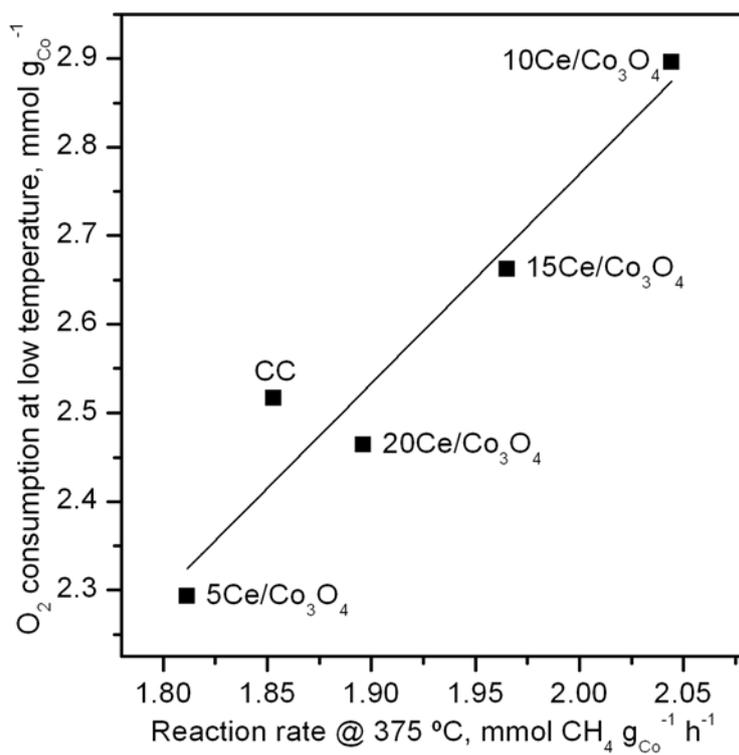
814

815   Figure 14